MESOPOROUS NITROGEN-DOPED CARBON-LiSICON GLASS CERAMICS AS HIGH PERFORMANCE CATHODES IN SOLID-STATE LITHIUM-OXYGEN BATTERIES (POSTPRINT)

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14. ABSTRACT
Here we report the use of N-C blend with 20 wt% LAGP (composite 3) in the cathode of a solid-state lithium-oxygen cell with superior discharge cell capacity compared to the cell performance with composite 1 and composite 2. The improvement in cell performance is due to the superior electrochemical activity of composite 3 for the reduction of oxygen and the higher ionic conductivity of LAGP to transport lithium ions in the composite matrix.

15. SUBJECT TERMS
lithium-oxygen battery, oxygen reduction reactions, nitrogen-doped carbon, lithium aluminum germanium phosphate

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Mesoporous Nitrogen-Doped Carbon-LiSICON Glass Ceramics as High Performance Cathodes in Solid-State Lithium–Oxygen Batteries

Padmakar Kichambare* and Stanley Rodrigues[a]

The vast increase in demand for energy has generated a large need for energy storage devices that have high energy and power densities. Among various electrochemical energy storage systems explored to date, the lithium–oxygen battery is one of the most promising technologies,[1] which is attracting a great deal of attention because of its high theoretical specific capacity.[2] Although these batteries offer many advantages, they also face many technical challenges that need to be overcome for the realization of practical lithium–oxygen cells operating in ambient environments. Several components dictate the performance of these cells, such as the oxygen cathode, electrolyte composition, relative humidity, and cell design.[3] In particular, the material architecture of the oxygen cathode plays a critical role for the reduction and diffusion of oxygen in the cathode of a lithium–oxygen cell.

In 1996, Abraham and Jiang[4] first reported a nonaqueous, rechargeable lithium–oxygen cell that delivered a cell capacity of 1410 mAh g^{-1} in a pure oxygen atmosphere. Following this work, there have been significant efforts to improve the cell capacity.[5] In our previous studies regarding solid-state, rechargeable lithium–oxygen cells,[6] we found that cells fabricated from carbon and lithium aluminum germanium phosphate (LAGP) demonstrated excellent discharge capacities. In subsequent work,[7,8] we reported an enhancement in discharge capacity for a cell prepared from a nitrogen-doped carbon (N–C) blend with 5 wt % LAGP (composite 1), and a N–C blend with 10 wt % LAGP (composite 2). In continuation, we report here the use of a N–C blend with 20 wt % LAGP (composite 3) in the cathode of a solid-state lithium–oxygen cell that demonstrates superior discharge cell capacity compared to the cell performance with composite 1 or 2. The improvement in cell performance is attributed to superior electrochemical activity of composite 3 towards the reduction of oxygen, and the higher ionic conductivity of LAGP to transport lithium ions throughout the composite matrix.

The morphology of composite 3 was examined by using SEM. Figure 1 shows the SEM image of composite 3, the image contains fibrous structures that correspond to the N–C blend, and crystals of LAGP (shown by the arrow). Typical Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption data and the mesopore size distribution at 77 K for composite 3 are shown in Figures S1 and S2, respectively (see the Supporting Information). The BET surface
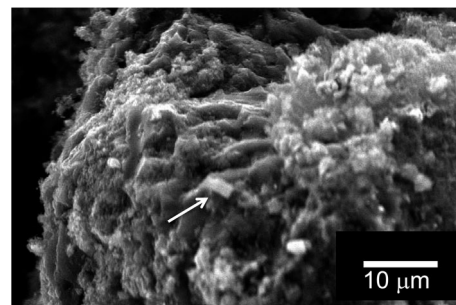
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Figure 1. SEM image of composite 3 (N–C blend and 20 wt % LAGP), which shows both fibrous and crystalline (see the arrow) material.

area, pore volume, and porosity of composite 3 were demonstrated to be 970 m^2 g^{-1}, 1.25 cm^3 g^{-1}, and 40.8 %, respectively.

Cyclic voltammetry (CV) was used to evaluate the electrocatalytic activity of composite 3. The CV curves recorded in an oxygen-saturated aqueous solution of 0.1 M KOH are presented in Figure 2, data for composite 1 and 2 are also shown for comparison. Well-defined oxygen reduction reaction (ORR) peaks were observed at approximately −0.495, −0.568, and −0.451 V versus a saturated calomel reference electrode (SCE), for composites 1, 2, and 3, respectively. The highest reduction current density of 0.0058 A cm^{-2} was obtained for composite 3. This indicates that in addition to a low carbon content and the lowest BET surface area, composite 3 also has the highest electrocatalytic activity for the ORR among all of the prepared composites. It is important to note that pure LAGP exhibits electrocatalytic activity towards the ORR,[9] and LAGP also displays high ionic conductivity. The existence of cavities and tunnels in the structure of LAGP accommodates gaseous oxygen molecules and
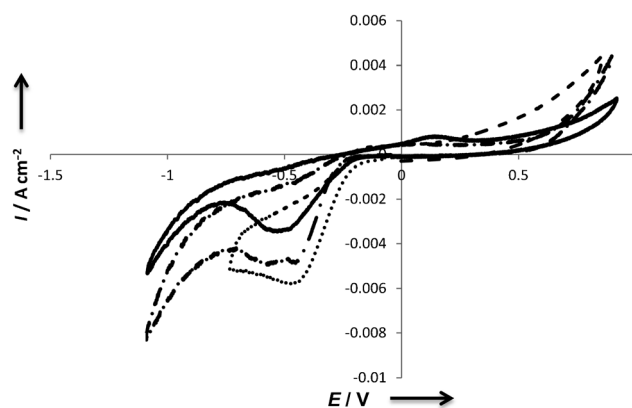

Figure 2. CV curves of composite 1 (——), composite 2 (–·–·), and composite 3 (·····) in 0.1 M KOH at 25 °C and a scan rate of 5 mV min^{-1}.

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aids the diffusion and reduction of oxygen at the cathode. LAGP could also aid in stretching the oxygen molecules, facilitating dissociation, while the N–C blend enhances the electronic conduction. Therefore, the combination of a N–C blend and LAGP in composite **3** affords highly active electrocatalytic sites, enhanced electronic and ionic conductivity, and potential stretching of the oxygen molecule, which together lead to enhanced electrocatalytic performance. Based on the high surface area of composite **3**, its mesoporous structure, and electrocatalytic activity towards oxygen reduction, a solid-state lithium–oxygen cell with a 2 cm² area was fabricated in the form of a coin cell. The cathodic side of the cell contained perforations so that oxygen could access the cathode. The lithium anode was coupled to an oxygen cathode through a solid electrolyte laminate, as described in our previous work.[6]

The charge–discharge profiles of the lithium–oxygen cell containing the composite **3** cathode, at various current rates, are shown in Figure 3. This cell was reversibly charged and discharged using currents of 0.2, 1, and 5 mA in an oxygen atmosphere at 75 °C. The open circuit voltages (OCV) of the lithium–oxygen cells fabricated with composites **1**, **2**, and **3** were 3.03, 2.92, and 2.91 V, respectively. The difference in OCV is likely because of internal series resistances between various cell components as well as activation polarization of the cathode. Solid-state cells fabricated with composite **3** exhibited reproducible charge–discharge characteristics. To stabilize the cells after fabrication, these cells were subjected to a conditioning cycle that used a small discharge and charge current of 0.05 mA. During this conditioning process, we observed minor transient behavior (voltage fluctuation) in some of the cells. This may be attributed to the existence of interfacial flaws during cell fabrication. As can be seen in Figure 3, a lithium–oxygen cell containing composite **3** delivered a high discharge cell capacity of 10.5 mAh at a discharge current of 0.2 mA. At higher discharge currents of 1 mA and

2 mA, the cell capacity of the lithium–oxygen cells decreased. However, the cells constructed with composites **1** and **2** as the cathodes delivered 1.97 and 9.03 mAh discharge capacities, respectively, at a discharge current of 0.2 mA.[7] Discharge capacities of 1.44 and 0.7 mAh for cells containing cathodes composed of only the N–C blend or a C blend, respectively, have been reported previously.[8] Our results are consistent with those of Kumar et al[6b], who reported data for incremental increases up to 77 wt % LAGP in a cathode formulation (containing a mixture of Ketjenblack and Calgon activated carbon powder). These studies indicated that an increase in LAGP loading increased the discharge capacity of the cell. In addition, an increase in LAGP loading also increased the total weight of the cathode and lowered the energy density of the cells. Thus, there is a compromise between the wt % of LAGP loading and the discharge cell capacity/energy density of the cell. Our efforts were aimed at achieving a higher cell capacity with a lower wt % of LAGP in the cathode formulation. The energy densities, normalized with the weight of the cathodes, for composites **1**, **2**, and **3** were found to be 891, 3714, and 4361 Wh kg⁻¹, respectively, at a discharge current of 0.2 mA. In the present work, the energy density of the cathode containing composite **3** represents a nearly 1.2-fold improvement compared to the energy density for composite **2**. Compared to the cathode composed with only the N–C blend, the cell with composite **3** has a cell capacity seven times greater. This enhancement in cell capacity is because of improved electrocatalytic activity, the high mesoporosity of composite **3**, and the fast lithium ion conduction deep inside the cathode. All of the characteristics of composite **3** are indicative of highly active electrocatalytic sites that can catalyze discharge reactions. In addition, a higher cathode porosity increases oxygen diffusivity throughout the cathode and increases accumulation of reaction products that help to improve the cell capacity. It is reported that pores of different sizes are filled with discharge products at different rates[10] until the oxygen electrodes cease functioning. Figure 3 also shows that there was a significant potential drop during the initial stage of discharge due to both an activation barrier of cathode chemistry that includes sluggish kinetics, and series resistances between various cell components.

In summary, this work demonstrates superior cell performance of lithium–oxygen cells with cathodes that are formed from a new material, composite **3** (a N–C blend and 20 wt % LAGP). The discharge capacity of this cell is 10.5 mAh, which is an order of magnitude higher than with a mesoporous carbon cathode. This work indicates the potential of composite **3** as a promising and low-cost cathode material for lithium–oxygen batteries.

Figure 3. The charge–discharge profiles for a lithium–oxygen cell using composite **3** as the cathode at discharge (D) and charge (C) currents of 5 mA (•••••), 1 mA (-----), and 0.2 mA (——).

Experimental Section

Fabrication of oxygen cathode

The working cathode, composite **3**, was prepared from a mixture of a N–C blend and 20 wt % LAGP (composites **1** and **2** con-
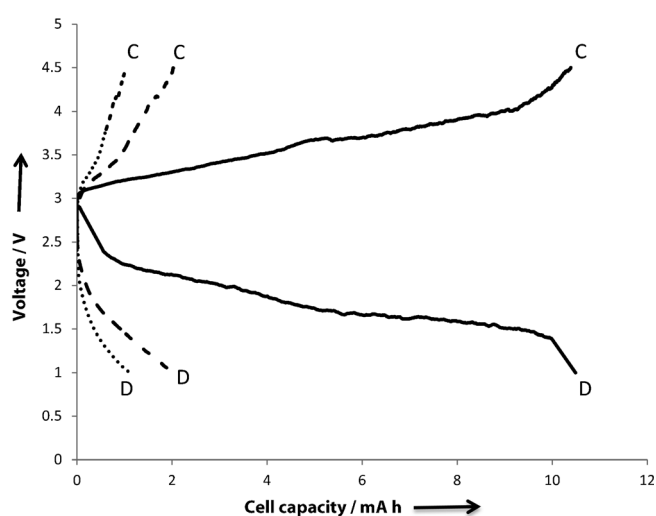
tained 5 and 10 wt % LAGP, respectively). The N–C blend was prepared from a mixture of nitrogen-doped Ketjenblack (N–KB) and nitrogen-doped Calgon activated carbon (N–CA) in a 40:60 wt % ratio. The N–C and LAGP powders were ball-milled with a polytetrafluoroethylene (PTFE) suspension and mixed with deionized water to obtain a soft mass. The solid pastes were spread onto nickel foams and pressed by sandwiching between two stainless-steel plates at 1 MPa. The cathode specimens were dried overnight at 100 °C under vacuum. Solid-state lithium–oxygen cells with a 2 cm^2 area were fabricated by using commercially available cell casing under a dry argon atmosphere. Each cell consisted of a composite film mounted onto a nickel foam that acted as the working cathode, lithium metal was used as the anode, and polymer-coated LAGP acted as the electrolyte.

Physical and electrochemical characterization

The morphology of the composite **3** powder was examined by using SEM. The BET surface area of composite **3** (Figure **S1**, see the Supporting Information) was obtained by using a nitrogen sorption instrument (Micromeritics ASAP 2020). The porosity of the cathode material was measured by using a gas pycnometer (Micromeritis, Accu Pyc II 1340). CV measurements were performed in a standard three-electrode cell configuration with 0.1 M KOH as the electrolyte, the CVs were measured at 25 °C with a scan rate of 5 mV min^{-1} by using a VersaSTAT 4 (Princeton Applied Research) electrochemical workstation. A paste that consisted of the N–C blend, 20 wt % LAGP, and Nafion (tetrafluoroethylene based fluoropolymer-copolymer) solution was prepared and spread onto the tip of a graphite rod, which was used as the working electrode. A Pt wire was used as the counter electrode and a SCE was used as the reference. The electrochemical performance of the solid-state lithium–oxygen cells fabricated with composite **3** was examined by using a computer-controlled VersaSTAT 4 electrochemical workstation. Charge–discharge measurements on these cells were performed in galvanostatic mode, and all measurements were performed under an oxygen atmosphere.

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